

SEMICONDUCTING PROPERTIES OF AISI 304 STAINLESS STEEL ANODIC FILMS FORMED AT DIFFERENT POTENTIALS

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INTRODUCTION

An understanding of the local structural and electronic properties of metal solid films is of technological interest in microelectronic and corrosion. The stainless steel electrodissoolution is very complex and the composition of the anodically formed layers depends on the electrolyte nature, potential disturbance program, anodization time and mass transport [1]. The polarization curves obtained under potentiostatic conditions exhibit a large range of passivity, followed by a depassivation region and, at more positive overpotentials, the passive state is accomplished. Previous works have been proposed that the passive layer is formed by a duplex film, with an outer Cr(III)-oxide/hydroxide layer grow at low potentials. At higher anodic potentials, the chromium dissolution takes place as CrO_4^{2-} ion and the electrode surface is covered by a Fe(III)-oxide/oxihydroxide film. Several authors have attempted to study semiconducting proprieties of passive films formed on stainless steel through the use of Mott-Schottky relation in comparison with photoelectrochemical studies. The role of crystallographic point defects in the semiconducting properties of compact anodic oxide films on metals has been discussed in detail in the point defect model (PDM) developped by Mac Donald et al [2]. The aim of this work is to investigate the semiconducting properties of anodically formed film on AISI 304 stainless steel in aerated oxalate solution, pH 5, at different potentials.

EXPERIMENTAL

Electrochemical measurements were carried out in a three-electrode conventional cell. The working electrodes consisted of a rotating disc made of stainless steel AISI 304 (from Goodfellow) with the following chemical composition (wt %): Ni 10, Cr 18, and balance Fe. Cyclic voltammograms and impedance measurements were conducted with the AISI 304 steel electrode in 1molL^{-1} aerated oxalate solution, pH 5. Potential measurements are referred to a saturated calomel electrode (SCE) provided with a Luggin capillary tip and the auxiliary electrode was Pt gauze.

RESULTS AND DISCUSSION

AISI 304 voltammogram in 1 M oxalate at static conditions, given in Fig.1, exhibits at the positive potential scan an anodic peak at -0.40 V followed by a large passive zone until 0.85 V. The reverse scan shows a small cathodic current peak at -0.25 V. The peak placed at 0.85 V can be ascribed to the Cr(III) oxidation reaction to chromate ion and the cathodic one, at -0.25 V, to the Cr(VI) to Cr(III) reduction occurring in the film. The current peaks are found to be independent of electrode rotation, suggesting that the reaction rate be limited by a solid-state electrooxidation process on the surface.

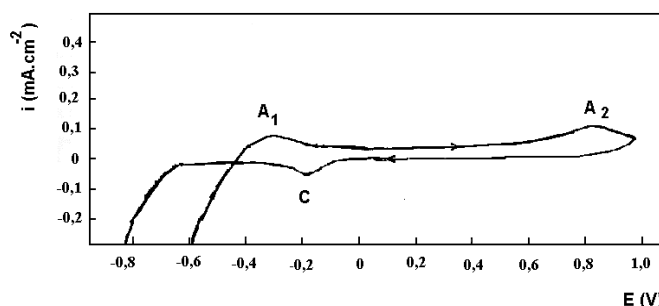


Figure 1.- Cyclic voltammograms for AISI 304 electrode in 1molL^{-1} aerated oxalate solution, pH 5, at 0.02V s^{-1}

In order to investigate the semiconducting properties EIS measurements were carried out at two different potentials. Firstly, the electrode was polarized at -0.20V during 30 minutes, region corresponding to a rich Cr_2O_3 passive layer. The EIS data were then collected every 0.10V, from -0.2 to 0.7V. A calculated Mott-Schottky plot is presented in Figure 2. The appearance of two distinct slopes indicates that the film behaves like a semiconductor n-type up to 0.4V. Between 0.4V and 0.7V a p-semiconducting layer is detected. This procedure was repeated by polarizing the electrode at 0.85V. Under this condition the surface is covered by a Fe-rich film. The corresponding Mott-Schottky plot is given in Figure 2 and a similar behaviour is found. These results can be explained based on the model proposed by Bujinov et al [3]. According these authors, the passive film can be represented as a donor of electrons, resulting in a n-type semiconductor. At high positive potentials, the negative defects (metal vacancies) injected at the film /solution interface play the role of electrons acceptors, resulting in a p-type semiconductor and enabling a transpassive dissolution. of Cr(III).

CONCLUSIONS

The anodic film formed on AISI 304 stainless steel at -0.20V and 0.85V is a n-type semiconductor in the lower potential and p-type in the higher potential region. It can be concluded that semiconducting properties of the passive films formed on AISI 304 steel in weakly acid solutions are governed by the rate of generation and transport of ionic point defects. These defects act as donor or acceptor species and are generated by chemical reactions at the interfaces with the substrate metal and the electrolyte.

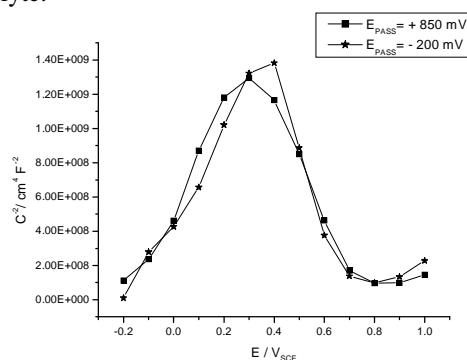


Figure 2 - Calculated Mott-Schottky plot for anodically formed film on AISI 304 in oxalate solution at $E = -0.2\text{V} (\star)$ and $E = 0.8\text{V} (\blacksquare)$.

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